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Characterization of Exhaust Emissions from a Dual Catalyst Equipped Vehicle

Environmental Sciences Research Lab, Research Triangle Park, NC

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CHARACTERIZATION OF EXHAUST EMISSIONS FROM A DUAL CATALYST EQUIPPED VEHICLE

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ABSTRACT

A test program was initiated to characterize exhaust gas emissions from an automobile equipped with a dual catalyst system. The dual catalyst system was designed by Gould, Inc. to reduce emissions of engine exhaust hydrocarbons, carbon monoxide, and nitrogen oxides. It basically consists of two catalysts in series: a nickel-copper alloy reduction catalyst to control carbon monoxide and hydrocarbon emissions.

The test vehicle, an AMC Hornet having a 232 CID six cylinder engine, was tested over the Federal Test Procedure, the Highway Fuel Economy Test, and the Sulfate Emission Test. In addition to the regulated gaseous emissions, sulfur dioxide, sulfuric acid, hydrogen cyanide, nickel carbonyl, carbonyl sulfide, aldehydes, and detailed hydrocarbon emissions were sampled and analyzed. A brief discussion of each method used to sample and analyze the non-regulated pollutants in included.

Results indicate that (1) sulfate emissions from the dual catalyst car were comparable to those from production catalyst vehicles equipped with air pumps, (2) hydrocarbon emissions were of low reactivity relative to other vehicles, and (3) nickel emissions were quite high. With regard to the nickel emissions, the forms in which this element are emitted are not known nor is the extent of nickel carbonyl emissions known.

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SECTION 1

INTRODUCTION

In an effort to comply with increasingly stringent emission standards, prototype automobiles have been equipped with different types of emission control equipment. While many approaches show promise in reducing the emissions of the regulated pollutants (HC, CO, and NO_x), these control systems should be examined for potential emissions of other harmful yet non-regulated gaseous and particulate pollutants.

One such control system which has shown promise in reducing regulated gaseous emissions from automobiles is the Gould dual catalyst system depicted in Figure 1. This system consists of a nickel-copper alloy

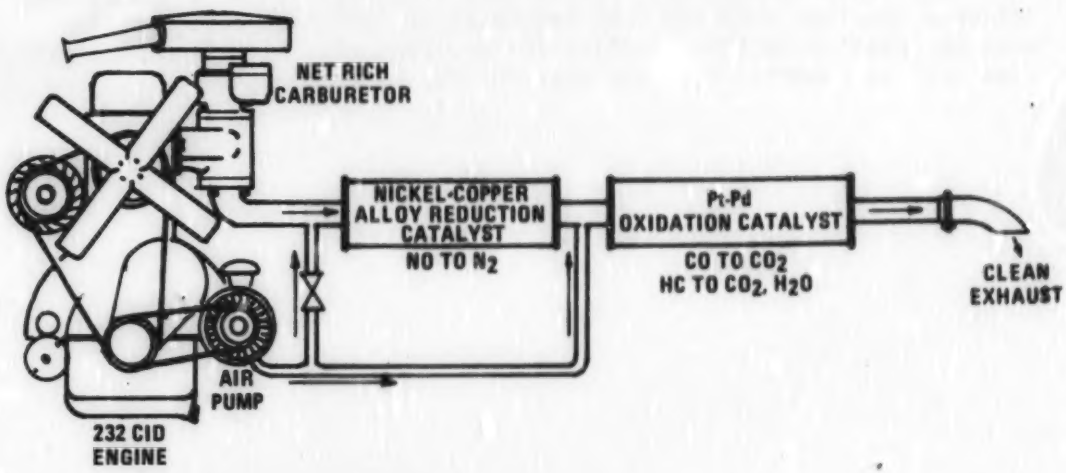

Figure 1. Schematic diagram of the dual catalyst system.

reduction catalyst followed in series by a platinum-palladium oxidation catalyst. The exhaust gases, containing hydrocarbons, carbon monoxide, and oxides of nitrogen, flow from the exhaust manifold into the reduction catalyst. In the reduction catalyst, under net reducing conditions, excess oxides of nitrogen are catalytically reduced forming molecular nitrogen. After exiting the reduction catalyst, the exhaust gases are mixed with injection air from the air pump. The air injection rate is carefully controlled to maintain a net oxidizing condition favorable for the catalytic oxidation of excess hydrocarbons and carbon monoxide. Proceeding into the oxidation catalyst, the hydrocarbon and carbon monoxide exhaust gases are heterogeneously oxidized to water vapor [$H_2O(g)$] and carbon dioxide [CO_2]. Small, carefully controlled quantities of air are likewise injected before the reduction catalyst to aid in system warm-up and in temperature maintenance. Carburetion is adjusted to control air-fuel ratios to 13.82 ± 0.18. Air-fuel ratio control to just slightly rich of stoichiometric is desired to provide a reducing atmosphere for the NO_x reduction catalyst while avoiding the overly rich mixture operation associated with poor fuel economy (1).

This paper examines the emissions from a Gould dual catalyst equipped automobile. In addition to the regulated emissions, non-regulated pollutants such as sulfuric acid, SO_2, nickel carbonyl, carbonyl sulfide (COS), aldehydes, hydrogen sulfide (H_2S), and hydrogen cyanide (HCN) were examined. Detailed hydrocarbon and aldehyde emissions measurements were also performed to evaluate the reactivity of those hydrocarbons being emitted. The methods employed for sampling and analysis of each of the non-regulated pollutants are also discussed.

This study represents a preliminary investigation of the emission patterns obtained from one dual bed catalyst prototype car. Further work to investigate the potential for environmental harm from such vehicles will be undertaken in the near future.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions have been made based on the experimental test program carried out on the Gould dual catalyst car:

1. Sulfate emissions measured over the Sulfate Emissions Test were comparable to those measured on production catalyst vehicles equipped with air pumps. Such vehicles represent the highest sulfate emitters presently in use.

2. Detailed hydrocarbon analyses demonstrated that hydrocarbon emissions from the Gould car were of a low reactivity relative to other vehicles tested at this facility.

3. Nickel emissions were significantly high, especially those measured on the first day of testing.

Although initial tests indicate the possible presence of nickel carbonyl in the dual catalyst vehicle's exhaust, some degree of analytical refinement coupled with further testing is required before any definite conclusions can be drawn regarding the emission of this compound. Immediate work should be directed towards the attainment of a firm conclusion with regard to this possible emission.

SECTION 3

EXPERIMENTAL PROCEDURES

EXPERIMENTAL EQUIPMENT

The dual catalyst system tested was installed on an AMC Hornet having a 232 CID six cylinder engine. A detailed description of the test vehicle is given in Appendix A. Upon arrival at this facility the odometer registered 12,500 miles. The observed spark timing was 5 degrees BTDC. Prior to dynamometer testing, the car was driven 500 miles over a mileage accumulation route for conditioning on the test fuel.

The "Raleigh Road Route", as the mileage accumulation route is termed, begins at the test laboratory, extends through the city of Raleigh, and returns to the test laboratory through the city of Durham. It is 51.8 miles long and has an averaged speed of 35 miles per hour. The route involves 20.7 expressway miles, 7.8 "suburban" miles, 23.3 miles on city streets, and an overall average of 0.62 stops per mile varying somewhat with traffic conditions. Considering the usual estimate of a 45 percent highway to 55 percent urban split for all U.S. driving, this route appears to be a reasonable representative mileage accumulation schedule. The schedule is repeated four times per day with half-hour cool-down periods between routes. Thus, the 500 miles were accumulated in 2-1/2 days.

A .030 weight percent sulfur fuel was used throughout the experiments. This sulfur level was attained by doping an unleaded test fuel with reagent grade Thiophene, C_4H_4S. Appendix B lists the fuel properties of the fuel used throughout the tests.

The experimental study was carried out in an automobile emissions laboratory equipped with a Clayton CT-50 water brake chassis dynamometer. Vehicle exhaust emissions were sampled for both particulate and gaseous pollutants in a combined dilution tunnel-constant volume sampler (CVS) arrangement (Figure 2). The diluent plus exhaust gas flow rate through the system was maintained at 407 ACFM. The particulate matter was sampled isokinetically in the dilution tunnel utilizing a four probe rake. The particles were collected on 47 mm filters in standard 47mm filter holders. Routine gas (HC, CO, CO_2, and NO_x) sampling and analysis was carried out in accordance with specifications given in the Federal Register.(2) Chassis dynamometer operation was also conducted in accordance with these specifications.

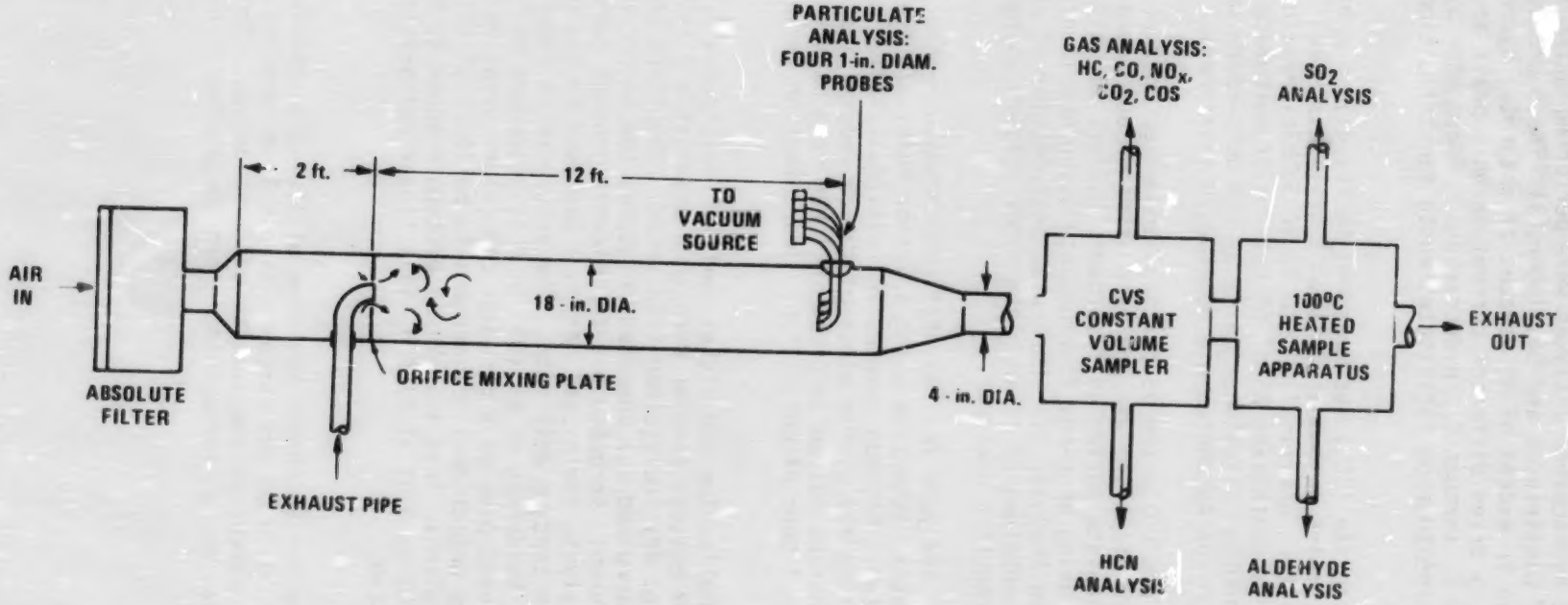

Figure 2. Sampling system.

ANALYSIS OF NON-REGULATED POLLUTANTS

Detailed hydrocarbon analyses were performed using the chromatographic procedures of Dimitriades and Seizinger.(3) These procedures permit quantification in excess of 95 percent of the total hydrocarbon being emitted. Fifty seven different chromatographic peaks are reported detailing the C_1 through C_{10} hydrocarbons. A computer system interfaced to the gas chromatograph facilitates rapid identification and quantification of the peaks.

Sulfur dioxide (SO_2) was measured in the dilute exhaust by pulling the gaseous samples into heated (100°C) stainless steel lines, through a Fluoropore filter, and finally into 50 cc bubble-breaking type fritted glass absorbers containing 25 ml of tetrachloromercurate solution. SO_2 was then determined colorimetrically by the West-Gaeke method using a modified Technicon Automated Air Monitor IV instrument.

Sulfate was collected as particulate matter on Fluoropore FA filters (1 micron pore size) and was analyzed using an automated barium chloranilate method. Particulate matter on fluoropore filters was also analyzed for trace metals using an x-ray fluorescence technique incorporating a 17 channel Siemen Analyzer.(4) Elemental analyses for %C and %H were performed upon samples obtained on 47 mm glass fiber filters using a Perkin-Elmer automated combustion analyzer.

Chemical analysis for COS utilized chromatographic separation and flame photometric detection using a Tracor Model 270HA atmospheric sulfur analyzer. Gaseous samples in individual Tedlar bags were continuously collected during all of the modes of the 75 Federal Test Procedure from the Scott constant volume sampler. All bag samples were run on the Tracor within 1 hour of collection. The detection level of COS was about 5 ppb.

Sample collection for nickel carbonyl utilized a heated two port manifold. Raw exhaust samples were then drawn at a 2 liter per minute flow rate into dry ice-acetone cold traps. The first cold trap, containing no solvent, scrubbed out unwanted moisture; the second cold trap, containing 50 ml of methanol, scrubbed out the nickel carbonyl component of the raw exhaust. Analysis for nickel carbonyl was done by gas chromatography with electron capture detection. The procedure is similar to that published by Sunderman et al.(5) In this procedure $Ni(CO)_4$ is separated from the solvent peak on a carbowax 20M column using 95:5 Argon-methane carrier. The detection limit appears to be .0001 µl $Ni(CO)_4$ per ml of collection solvent. This analytical procedure seems to have an application range of 0.001 to 0.01 µl $Ni(CO)_4$ as a linear calibration range for this detector system.

Sampling for aldehydes was done utilizing a stainless steel sample line in a CVS diluted gas stream. Sample line temperature was maintained at 100°F to prevent polymerization of formaldehyde. This diluted exhaust gas sample was passed through impingers containing a solution of 2, 4-

dinitrophenylhydrazine (DNPH) in HCl. Carbonyls present in the sample stream react with the absorbing reagent forming soluble and insoluble hydrazone derivatives which are removed by filtration and extraction techniques. Aldehyde characterization is then completed using a single gas chromatographic analysis.

Hydrogen cyanide (HCN) was measured in the dilute exhaust by passing the gaseous samples through series impingers containing a 0.3N NaOH Epstein's procedure (6) using a Technicon Autoanalyzer integrated with a Varian 635D spectophotometer having a 1.0 cm automatic flow cell.

Wet chemical techniques were used to determine H_2S emission over the 75 FTP runs. Bubbler samples obtained from CVS dilute exhaust were collected in impingers containing 15 cc of absorbing solution (zinc hydroxide stabilized with ammonium sulfate and glycerin) and analyzed by the methylene blue method (7). Standards prepared from permeation tubes were used to qualify the sample collection method (8). Absorbing solutions containing known amounts of H_2S showed some loss on exposure to auto exhaust. An effective detection limit of 0.6 μ H_2S per sample was indicated.

SECTION 4

RESULTS AND DISCUSSION

ROUTINE GASEOUS AND PARTICULATE DATA

Routine gaseous and particulate sampling and analyses were conducted during an initial test series performed on the dual catalyst car. Runs within these series were sequenced over two days of testing. The daily test sequence was as follows: one 75 Federal Test Procedure (FTP), two Sulfate Emission Tests (SET), two Highway Fuel Economy Tests (HWFET), and two more SET's.

Subsequent FTP's were run to obtain additional information about detailed hydrocarbons, H_2S, HCN, COS, aldehydes, and nickel carbonyls. Also, two final FTP runs were obtained for routine gaseous analysis when it was discovered that the inertia settings on previous runs had been set 500 pounds too high. Such an error is expected to have affected the gaseous emissions data and as it turned out, the HC, CO, and NOx emissions were about 8, 47, and 26 percent lower, respectively. The fuel economy was found to be only about three percent higher.

The complete gaseous emissions data is presented in Tables 1 and 2. Run numbers over 5378 were conducted following the initial two day test program described above. The average values are indicated by the $\bar{x}$ symbol and are shown at the bottom of each data set. The data set labeled "3500 lb. inertia load" covers those tests for which the inertia load was set as prescribed in the Federal Register.

EPA Ann Arbor had previously tested this same car for gaseous and sulfate emissions. Their HC, CO, and NOx emission rate measurements were 0.18, 2.74, and 0.34 gm/Km, respectively. These HC and NOx values compare fairly well with the 0.14 and 0.37 gm/Km levels reported here. Their CO level is closer to the 1.41 gm/Km. level meausred at this lab while testing at the heavier inertia loadings. The low CO measurements recorded at the correct inertia setting should be viewed with some caution because only two data points were obtained at this setting.

The oxidation catalyst appeared very active as evidenced by the extremely low CO and HC emission rates. The reduction catalyst was effective in reducing the NOx emissions to about 0.37 grams per kilometer over the FTP runs with the 3500 lb. inertia loading. Even at higher inertia loadings NOx emissions were quite low, the average being about 0.50 gm/Km.

Table 3 lists the sulfur dioxide, sulfate and particulate emission rates from each of the tests conducted. Of primary interest are the sulfate results from the SET runs. High sulfate emissions were expected because of high oxidation catalyst activity in conjunction with high O_2 levels in the exhaust preceding the catalyst. The average sulfate emission rate for the SET was 23.8 mg/Km. with the sulfate material comprising approximately 51 percent of the total particulate matter emitted. EPA-Ann Arbor has reported an SET sulfate emission rate of 22.5 mg/Km. for this same vehicle. This sulfate emission rate is greater than that of the average production catalyst vehicle not equipped with an air pump.

TABLE 1. GASEOUS EMISSION RESULTS
FTP GASEOUS EMISSIONS
(gm/km)

4000 lb. INERTIA LOAD

RUN #	HC	CO	NO_x	km/l
5365	0.162	1.710	0.485	6.52
5372	0.158	1.282	0.534	6.27
5404	0.161	1.519	0.439	6.31
5407	0.189	1.915	0.509	6.12
5408	0.124	1.230	0.577	6.35
5411	0.149	1.014	0.470	6.56
5432	0.158	1.223	0.504	6.11
5433	0.155	1.406	0.512	6.77
$\bar{X}$	0.157	1.413	0.504	6.37
	(0.251 gm/mi)	(2.261 gm/mi)	(0.806 gm/mi)	(15.06 mpg)

3500 lb. INERTIA LOAD

5434	0.149	0.816	0.403	6.73
5435	0.139	0.681	0.345	6.33
$\bar{X}$	0.144	0.749	0.374	6.53
	(0.230 gm/mi)	(1.198 gm/mi)	(0.598 gm/mi)	(15.44 mpg)

TABLE 2. GASEOUS EMISSION RESULTS

HWFET GASEOUS EMISSIONS (gm/km)

RUN #	HC	CO	NO_x	km/l
5368	0.089	0.091	0.135	9.09
5369	0.134	0.199	0.146	9.16
5375	0.069	0.090	0.107	9.55
5376	0.096	0.090	0.143	9.22
$\bar{X}$	0.098	0.118	0.133	9.25
	(0.156 gm/mi)	(0.188 gm/mi)	(0.213 gm/mi)	(21.87 mpg)

SET GASEOUS EMISSIONS (gm/km)

5366	0.066	0.126	0.351	8.48
5367	0.091	0.126	0.176	8.44
5370	0.204	0.126	0.204	8.32
5371	0.068	0.126	0.223	8.32
5373	0.146	0.126	0.524	8.84
5374	0.064	-	0.554	8.57
5377	0.064	-	0.431	8.34
5378	0.084	0.136	0.361	7.69
$\bar{X}$	0.098	0.128	0.353	8.38
	(0.157 gm/mi)	(0.204 gm/mi)	(0.565 gm/mi)	(19.80 mpg)

TABLE 3. SO_2, SO_4, AND PARTICULATE MATTER EMISSIONS RESULTS

FTP EMISSIONS

RUN #	SO_2 gm/km	FUEL S AS SO_2 %	PARTICULATE mg/km	SO_4 mg/km	SO_4/PARTICULATE %	FUEL S AS SO_4	TOTAL SULFUR BALANCE
5365	0.011	15.7	11.1	2.1	18.6	2.0	17.7
5372	0.021	30.4	28.8	12.6	43.6	11.9	42.3
$\bar{X}$	0.016	23.0	19.9	7.3	31.1	6.9	30.0
	(0.026 gm/mi)		(31.9 mg/mi)	(11.7 mg/mi)			

HWFET EMISSIONS

5368	0.026	55.9	32.4	16.8	51.7	23.5	79.4
5369	0.029	60.7	29.9	15.4	51.4	21.3	82.0
5375	0.025	54.1	49.3	23.9	48.5	34.5	88.6
5376	0.025	52.6	5.1	23.9	47.5	34.0	86.6
$\bar{X}$	0.026	55.8	40.6	20.8	49.8	28.3	84.1
	(0.042 gm/mi)		(65.0 mg/mi)	(32.0 mg/mi)			

SET EMISSIONS

5366	0.031	60.5	23.8	14.5	60.9	18.6	79.1
5367	0.019	37.1	29.9	15.8	52.8	21.3	57.4
5370	0.028	53.3	34.3	17.7	51.7	22.2	75.5
5371	0.031	57.2	40.6	20.8	51.1	28.0	85.1
5373	0.023	45.6	72.3	33.6	46.4	45.3	90.9
5374	0.019	37.8	70.0	33.9	48.3	44.8	81.8
5377	0.020	38.1	61.2	29.1	47.6	36.9	75.0
5378	0.023	40.2	51.3	24.7	48.2	28.6	68.8
$\bar{X}$	0.024	46.2	47.9	23.8	50.9	30.5	76.7
	(0.039 gm/mi)		(76.7 mg/mi)	(38.0 mg/mi)			

TABLE 4. ELEMENTAL ANALYSIS OF PARTICULATE MATTER

TEST CYCLE	% C*	C-mg/km (mg/mi)	% H*	H-mg/km (mg/mi)
FTP	3.2	0.64 (1.02)	4.8	0.96 (1.53)
SET	3.9	1.61 (2.57)	2.0	0.81 (1.23)

*VALUES REPRESENT THE PERCENTAGE OF COMPONENT CONCENTRATION WITHIN THE PARTICULATE MATTER SAMPLED.

The quantity of carbonaceous material contained within the particulate matter examined was quite small. Table 4 shows the results of combustion analyses for percent carbon and hydrogen content and the low carbon percentages are apparent. At first glance the hydrogen content might appear high, but these values reflect the amount of water in combination with high levels of sulfuric acid present.

DETAILED HYDROCARBON AND ALDEHYDE EMISSIONS

The detailed hydrocarbon emission rates for the FTP are given in Table 5. The values reported are the means of three tests. The gm/Km emission rates for each hydrocarbon are calculated utilizing the actual density of each specific compound (i.e. methane: 18.86 gm/cu. ft., ethylene: 16.51 gm/cu ft., acetylene: 15.33 gm/cu. ft., etc) rather than 16.33 gm. cu. ft. average density specified in the Federal Register. The Federal Register value is based on an average hydrocarbon molecule having a hydrogen to carbon ratio of 1.85. However, with detailed chromatographic information available, the actual hydrocarbon molecule is known and the density for each respective compound can be accurately calculated.

To permit discussion of the photochemical reactivity of the emissions, the compounds were subdivided into four basic reactivity groupings. These groupings have been suggested by Dimitriades (9) with relative reactivity ratings as follows:

	Class	Relative Molar Reactivity Rating (normalized to Class I)
I.	(Nonreactive) C_1-C_3 paraffins, acetylene, benzene	1.0
II.	(Reactive) C_4+ paraffins	6.5
III.	(Reactive) aromatics less benzene	9.7
IV.	(Reactive) olefinics	14.3

For this vehicle 29.5 percent of the total mass emitted was Class I, 49.6 percent Class II, 13.3 percent Class III, and 7.6 percent Class IV. This compares very favorably with other vehicles previously tested. (10) Table 6 shows the comparison with several other vehicles and emission control systems. It is apparent that the relative abundance of olefinic and aromatic hydrocarbons is significantly less. Also of significance is the finding that of the total hydrocarbon mass emitted, 24.8 percent was methane.

TABLE 5. FTP DETAILED HYDROCARBON EMISSIONS

Peak No.	Compound	gm/Km.
1	Methane	.0484
2	Ethylene	.0069
3	Ethane	.0069
4	Acetylene	.0024
5	Propylene; Propane	.0030
6	Propadiene	.0002
7	Methyl acetylene	ND
8	Isobutane	.0009
9	Butene 1; isobutylene	.0019
10	N-butane; 1, 3-butadiene	.0149
11	Trans-2-butene	.0009
12	Cis-2-butene	.0002
13	3-methyl-1-butene	.0001
14	Isopentane	.0175
15	Pentene-1	ND
16	N-pentane; 2-methyl-1-butene	.0121
17	Trans-2-pentene	.0004
18	Cis-2-pentene	.0004
19	2-methyl-2-butene	.0064
20	Cyclopentane;3-methyl-1-pentene	.0185
21	2,3-dimethylbutane	.0014
22	2-methylpentane; 2,3-dimeth-1-butene	.0005
23	3-methylpentane	.0002
24	1-hexene;2-ethyl-1-butene	.0006
25	N-hexane; cis-3-hexene	.0002
26	2 methyl-2-pentene	.0005
27	Methylcyclopentane; 3-methtrans-2-pentene	.0002
28	2,4-dimethylpentane	ND
29	Methylcyclopentene	.0022
30	Benzene, cyclohexane	.0061
31	Cyclohexene; 2,3-dimethylpentane; 2-methylhexane	.0014
32	3-methylhexane	.0110
33	Iso octane	.0014
34	N-heptane	.0007
35	Methylcyclohexance	.0025
36	2,4 and 2,5-dimethylhexane	.0012
37	2,3,4-trimethylpentane	ND
38	2,3,3-trimethylpentane	.0107
39	Toluene; 2,3-dimethylhexane	.0018
40	2-methylheptane	.0015
41	3-methylheptane	.0002
42	2,2,5-trimethylhexane	.0014
43	N-octane	.0001
44	2,3,5-trimethylhexane	.0001
45	2,4-dimethylheptane	.0002
46	2,5 and 3,5-dimethylheptane	.0006
47	Ethylbenzene; 2,3-dimethylheptane	.0014
48	P-xylene; m-xylene, 4-methyloctane	.0008
49	O-xylene; unk C_9 paraffin	.0001
50	Nonane	.0001
51	N-propylbenzene	.0005
52	1-methyl 3-ethyl-benzene; unk C_{10} paraffin	ND
53	1-methyl-2-ethylbenzene; unk C_{10} paraffin	ND
54	Mesitylene	ND
55	1,2,4-trimethylbenzene	.0001
56	Secbutylbenzene; n-decane	.0019
57	Unknowns	.1953 ± .0184
	TOTAL	(.3125 gm/mi)

TABLE 6. COMPARISON OF EXHAUST HC REACTIVITIES

VEHICLE	CONTROL SYSTEM	HC* gm/km (gm/mi)	PERCENTAGE OF TOTAL			
			CLASS I	CLASS II	CLASS III	CLASS IV
AMC HORNET PROTOTYPE	DUAL CATALYST W/ AIR PUMP	0.19 (0.31)	29.5	49.6	7.6	13.3
1975 CHRYSLER IMPERIAL PROTOTYPE 440 CID	ELECTRONIC LEAN BURN	0.23 (0.36)	18.8	23.8	17.8	39.6
1975 FORD GRANADA 302 CID	SINGLE MATTHEY-BISHOP OX-CAT. W/ AIR PUMP	0.34 (0.55)	21.7	39.1	18.8	20.4
1975 CHEV. IMPALA 350 CID	AC OX-CAT.	0.16 (0.25)	22.1	39.2	18.2	20.4
1975 PLY. FURY 318 CID	UOP OX-CAT.	0.31 (0.49)	13.8	50.9	18.0	17.3

*BASED ON SUMMATION OF DETAILED HYDROCARBON EMISSION RATES.

Aldehyde emission results are listed in Table 7. The present GC analytical system is incapable of separating acetone, acrolein, and propionaldehyde because all have approximately the same retention times, therefore, these emissions are all calculated on the basis of an acetone emission. Sampling for aldehydes was conducted over three FTP's with the mean emission of total aldehydes being .01725 gm/Km. This value compares favorably with prototype lean burn, catalyst, and CVCC vehicles tested to date. Aldehyde emissions from these vehicles are also included in Table 7 for comparison purposes.

Of interest is the apparent trend in aldehyde emissions over the three tests conducted. Although formaldehyde emissions remain essentially constant over the tests, the other aldehyde emissions are seen to decrease. No explanation is available for this trend and it is unfortunate that further testing to elicit some clarification could not have been completed because of time restrictions.

EMISSIONS OF COS, H_2S, $Ni(CO)_4$, AND HCN

Three separate FTP's for COS collection were run on the dual catalyst car and results indicate that COS was present at concentrations not greater than 5 ppb. Most of the COS present occurred during the cold start mode (bag 1) of the FTP. It was found that COS did not react with auto exhaust in dilution tunnel injection experiments in which equal concentrations of COS injected into the tunnel both with and without auto exhaust present gave identical COS recoveries from bag samples. The COS concentration in the bag samples remained stable for at least 24 hours.

No H_2S was detected in the CVS diluted exhaust gas in any of the FTP runs conducted. H_2S detection limits of 0.6 µg per sample correspond to a concentration of 34 ppb during Bag 1 of the FTP. Bag 1 is most crucial from the standpoint of H_2S formation in catalyst vehicles because of the lower temperature and richer operating conditions associated with cold starts and warmups.

Analyses for nickel carbonyl were performed utilizing a gas chromatographic separation and electron capture detection. Results indicate that a strong electron-absorbing species is present at a retention time very close to that of nickel carbonyl. However, additional experimentation needs to be performed before it can be stated conclusively that this component is in fact nickel carbonyl. It is highly possible that an interference problem exists from some unknown component.

Collection and measurement for HCN was conducted over two FTP cycles. The HCN emissions which were measured over each test are shown in Table 8. HCN emissions from the Chryslers and Honda CVCC are also included for comparison purposes and these test results indicate that HCN emissions from the dual catalyst vehicle are lower.

TABLE 7. FTP ALDEHYDE EMISSIONS - mg/km

VEHICLE/ RUN #	FORM-ALDEHYDE	ACET-ALDEHYDE	ACETONE/ ACROLEIN/ PROPION-ALDEHYDE	CROTON-ALDEHYDE	HEXAN-ALDEHYDE	BENZ-ALDEHYDE	TOTAL
AMC HORNET DUAL CATALYST:							
5404	4.51	3.28	15.64	0.15	0.54	2.93	27.04
5407	4.11	1.76	6.56	ND	ND	1.54	13.98
5408	4.76	0.91	3.76	ND	0.18	1.22	10.83
$\bar{X}$ mg/km	4.46	1.98	8.66	0.15	0.36	1.89	17.25
(mg/mi)	(7.13)	(3.17)	(13.85)	(0.24)	(0.58)	(3.03)	(27.6)
1975 CHRYSLER 440 CID, LEAN BURN	25.88 (41.40)	7.94 (12.70)	7.06 (11.30)	2.30 (3.68)	0.16 (0.26)	5.36 (8.57)	46.13 (73.80)
1975 HONDA CVCC	10.61 (16.97)	3.18 (5.08)	3.27 (5.23)	0.72 (1.16)	0.16 (0.26)	1.96 (3.14)	19.90 (31.84)
1975 FORD W/ OX-CAT.	19.56 (31.30)	4.38 (7.00)	11.00 (17.61)	ND	4.13 (6.59)	5.75 (9.21)	43.38 (69.40)

TABLE 8. FTP HYDROGEN CYANIDE EMISSIONS

VEHICLE/ RUN #	HCN EMISSION mg/km (mg/mi)
AMC HORNET DUAL CATALYST:	
5432	3.96 (6.33)
5435	1.59 (2.55)
$\bar{X}$	2.78 (4.44)
1975 CHRYSLER 440 CID LEAN BURN - 242	6.38 (10.20)
1975 CHRYSLER 440 CID LEAN BURN - 251	7.13 (11.40)
1975 HONDA CVCC	7.19 (11.51)

X-RAY FLUORESCENCE ANALYSIS

X-ray fluorescence analysis of particulate samples was performed to determine the extent of trace element emissions. The summarized results are listed according to test cycle in Table 9. The filters from which this data was extracted were collected during each of the tests conducted over the first two days of testing. The only elements having significant emission rates were nickel, sulfur, and iron. When it is assumed that the sulfur is emitted as $H_2SO_4 \cdot 5H_2O$ and the iron as Fe_2O_3, the total mass of particulate matter emitted over each of the three test cycles (Table 3) can nearly be accounted for.

Nickel emissions were prominent in the FTP runs. On the very first FTP the nickel emission rate 4.38 mg/Km., an emission equal to 40 percent of the total particulate matter emitted. On later tests the rate was observed to trail off. Nonetheless, these rates are much higher than those observed when testing other vehicles at this facility and it would appear that the nickel alloy reduction catalyst is the source of this emission.

Iron emissions were only of significance over the FTP runs. High iron oxide emissions occur during the FTP because exhaust gas fluctuations are more severe than during the other test cycles. This sort of finding is consistent with data reported on catalyst car emissions by Braddock (11).

TABLE 9.
X-RAY ANALYSIS SUMMARY

ELEMENT	FTP[1] mg/km (mg/mi)	SET[2] mg/km (mg/mi)	HWFET[3] mg/km (mg/mi)
Pb	0.11 (0.18)	0.04 (0.07)	0.02 (0.03)
Si	0.08 (0.12)	0.02 (0.03)	0.02 (0.03)
Al	0.03 (0.05)	0.01 (0.01)	0.01 (0.01)
S	2.54 (4.07)	7.09 (11.35)	6.26 (10.01)
Cu	0.08 (0.12)	0.01 (0.02)	0.01 (0.01)
Ni	2.58 (4.12)	0.31 (0.50)	0.17 (0.27)
Fe	0.35 (0.56)	0.04 (0.07)	0.02 (0.03)
Cl	0.02 (0.03)	ND	ND

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APPENDIX A

Test Vehicle Description
Prototype AMC Hornet Dual Catalyst Car

Engine

type	in-line 6 cyl., spark ignition
bore x stroke, cm x cm (in x in)	9.525 x 9.893 (3.75 x 3.89)
displacement, cc (in^3)	4228 (258)
compression ratio	7.95:1
maximum power @ rpm, Kw (Hp)	74.57 (100) @ 3600 rpm.
fuel metering	gasoline

Drive Train

transmission	automatic
final drive ratio	3.08

Chassis

type	front engine, rear wheel drive
tire size	695 x 14
inertia weight	3500 lbs.
passenger capacity	5

Emission Control System

basic type	Engelhard II B oxidation catalyst, Gould GEM 68 reduction catalyst, air pump, and EGR.

APPENDIX B

Unleaded Gasoline Analysis

Research Octane Number	93.2
Motor Octane Number	84.7
Reid Vapor Pressure, psia	10.2

Distillation, AST, D-86, °F

IBP	90
10%	124
50%	203
90%	290
EP	372

FIA Analysis

Aromatics %	24.0
Olefins %	8.3
Paraffins %	67.7

API Gravity @ 60°F	61.6

Weight % C	85.26
Weight % H	14.01
Weight % S	0.020
Lead, gm/gallon	.00004